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THE POSITIONS OF THE HYDROGEN ATOMS IN ALLYLLITHIUM AND SOLVATED ALLYLLITHIUM SPECIES. A MNDO STUDY

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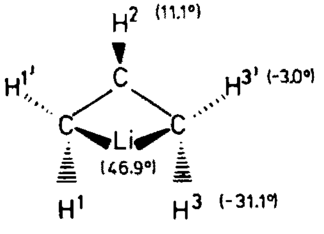
Summary

In the MNDO geometry optimized structures of allyllithium and the solvated species $C_3H_5Li \cdot 2H_2O$ and $C_3H_5Li \cdot 3H_2O$ the allyl portions are distorted from planarity: the inner hydrogens H^1 and H^3 are strongly bent away from the lithium atom while the central hydrogen H^2 is only slightly bent towards lithium. This confirms earlier ab initio calculations on C_3H_5Li but disagrees with recent proposals, based on ^1H and ^{13}C NMR investigations of allyllithium in tetrahydrofuran, that H^2 is much more bent out of the plane of the carbon atoms than H^1 and H^3. X-ray structural data for the distorted allyl moiety exist only in the case of $(\eta^3\text{-}C_3H_5)_2NiP(CH_3)_3$ and $C_6H_8Li_2 \cdot 2TMEDA$; they support the calculated data.

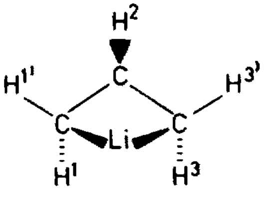
After it had been shown experimentally that allyllithium in tetrahydrofuran (THF) forms a bridged [1a–1c] monomeric [1b] π-complex, further studies on the structure of allyllithium must focus on the positions of the hydrogen atoms.

According to ab initio calculations (Schleyer and his colleagues [2]) on C_3H_5Li (corresponding to a monomer in the gas phase) the inner hydrogens H^1 and H^3 are



ab initio (≙monomeric in the gasphase)[2]

(1a)



NMR in THF[4]

(1b)

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much more bent out of the plane of the carbon atoms (away from lithium; out of plane angle −31.1°) than the central H^2 (towards lithium; out of plane angle 11.1°), s. **1a**. The outer hydrogens $H^{1'}$ and $H^{3'}$ are only weakly bent out of the plane (−3.0°).

Schlosser and Stähle, on the other hand, on the basis of ^1J(C,H) and ^3J(H,H) coupling constants proposed structures such as **1b** for C_3H_5M (M = Li, Na, K) in THF [4]. In **1b** it is the central hydrogen H^2 which is bent out of the plane of the carbon atoms (towards lithium) more than the inner hydrogens H^1 and H^3 (away from lithium). The outer hydrogens $H^{1'}$ and $H^{3'}$ remain in the plane of the carbon atoms.

A recently published X-ray structure determination of the *N,N,N,N*-tetramethylethylenediamine (TMEDA) complex of C_3H_5Li revealed a polymeric chain structure $(\ldots C_3H_5[LiC_3H_5]_nLi\ldots)$ which did not allow a determination of the positions of the hydrogen atoms [5], and accordingly a decision between **1a** and **1b**. Therefore we performed a MNDO study [6] on C_3H_5Li, $C_3H_5Li \cdot 2H_2O$ and $C_3H_5Li \cdot 3H_2O$. It seemed necessary to include the solvated species $C_3H_5Li \cdot 2(3)H_2O$ in a comparison of calculated structures with the structural proposal **1b** [4] because (a) **1b** is derived from C_3H_5Li in THF, in which it is solvated and; (b) calculations of unsolvated and solvated lithium compounds may lead to entirely different structures as shown for the phenyllithium dimer [7].

The MNDO heats of formation (kcal mol^{-1}) of the geometry optimized structures given in Table 1 are of interest wih regard to the question of the stability of planar (I, III) versus non-planar (II, IV, V) and unsolvated (I, II) versus solvated (III, IV, V) species.

The following conclusions can be drawn from Table 1:

(a) The non-planar II and IV are more stable than their planar counterparts I and III; this has been attributed to the better interaction between the $p\pi$ orbitals of C^1, C^3 and lithium in the non-planar structures II and IV [2]. The bending of the central hydrogen atom H^2 towards lithium is caused by the "inward" bending of the $p\pi$ orbital at C^2, which allows better overlap with the orbitals at C^1 and C^3.

(b) The importance of solvation is clearly seen if the heats of formation of the H_2O molecules in III, IV and V ($\Delta H_f(H_2O)$) are subtracted from the heats of formation of the latter species (ΔH_f) yielding the differences $\Delta\Delta H_f = \Delta H_f - \Delta H_f(H_2O)$ (Tab. 1). The values used for $\Delta H_f(H_2O)$ refer to the calculated geome-

TABLE 1

MNDO HEATS OF FORMATION (kcal mol^{-1}) OF THE ALLYLLITHIUM SPECIES I–V (OPTIMIZED GEOMETRIES)

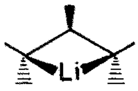
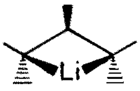
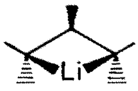
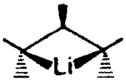
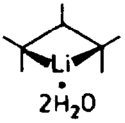
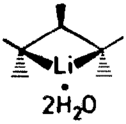
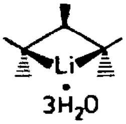
	 (I)	 (II)	 $\cdot$ $2H_2O$ (III)	 $\cdot$ $2H_2O$ (IV)	 $\cdot$ $3H_2O$ (V)
ΔH_f	10.2	0.08	−141.0	−149.4	−209.9
$\Delta\Delta H_f$	–	–	−19.2	−27.6	−27.1

TABLE 2

MNDO OPTIMIZED GEOMETRIES AND CHARGES OF I–V

	 (I)	 (II)	 $\cdot 2H_2O$ (III)	 $\cdot 2H_2O$ (IV)	 $\cdot 3H_2O$ (V)
Bond lengths (pm)					
C^1–C^2	141.5	142.6	141.0	142.0	141.3
C^1–C^3	251.7	251.7	252.4	252.6	252.3
Li–C^1	212.9	205.6	220.9	213.2	221.6
Li–C^2	205.6	208.7	211.2	212.6	217.3
Li–O^1	–	–	215.7	216.3	227.3
Li–O^2	–	–	216.0	215.5	221.5
H^2–C^2	110.4	110.2	110.5	110.3	110.5
$H^{1'}$–C^1	109.0	109.5	109.1	109.5	109.4
H^1–C^1	111.1	111.1	110.5	110.5	110.2
Bond angles (°)					
C^1–C^2–C^3	125.7	123.9	127.0	125.6	126.4
H^2–C^2–C^1	117.2	117.8	116.5	117.0	116.7
$H^{1'}$–C^1–C^2	121.2	118.8	121.0	118.9	119.5
H^1–C^1–C^2	124.8	120.9	124.9	121.6	122.1
C^1–Li–C^2	39.5	40.3	38.0	39.0	37.6
C^1–Li–C^3	72.5	75.5	69.7	72.7	69.4
O^1–Li–O^2	–	–	101.3	101.1	83.9
O^1–Li–O^3	–	–	–	–	99.9
C^1–Li–O^1	–	–	121.3	121.5	95.5
C^1–Li–O^2	–	–	121.4	120.1	149.1
C^1–Li–O^3	–	–	–	–	110.6
C^2–Li–O^1	–	–	113.0	115.3	115.9
C^2–Li–O^2	–	–	145.7	143.6	115.9
C^2–Li–O^3	–	–	–	–	130.7
Out of plane angles (positive = above, negative = below the $C^1C^2C^3$ plane)					
H^2–C^2 [°]	0.0	+7.4	0.0	+6.6	+4.5
$H^{1'}$–C^1	0.0	+1.0	0.0	0.0	−2.7
H^1–C^1	0.0	−29.9	0.0	−27.1	−24.7
Li–C^2	+50.4	+39.4	+53.8	+43.8	+49.6
Charges					
C^1	−0.396	−0.362	−0.396	−0.350	−0.380
C^2	0.081	0.108	0.093	0.106	0.112
H^1	0.045	0.048	0.024	0.028	0.020
$H^{1'}$	0.051	0.054	0.045	0.016	0.010
H^2	0.042	0.032	0.025	0.043	0.033
C_3H_5	−0.479	−0.395	−0.535	−0.449	−0.542
Li	0.479	0.395	0.225	0.138	0.147

tries of H_2O in III–V, and differ by less than 0.03 kcal mol^{-1} from the optimized value for free H_2O.

Thus:

(i) In the case of the planar I and III solvation by $2H_2O$ leads to a 29.4 kcal mol^{-1} stabilization of the C_3H_5Li component;

(ii) In the case of the non-planar II and IV the stabilization (27.6 kcal mol^{-1}) is slightly smaller by 1.8 kcal mol^{-1}. This results from the weaker σ-donor and π-acceptor qualities of bent versus planar C_3H_5Li towards H_2O;

(iii) Addition of a third H_2O molecule (V) does not lead to an increase in stability of the C_3H_5Li component, which agrees well with experimental results: the lithium atom is generally tetracoordinated [8].

Geometries and charges of I–V are listed in Table 2.

The most important finding is that in the solvated (IV, V) allyllithium species, as in the unsolvated II, [2], H^1 and H^3 are much more bent out of the plane of the carbon atoms than H^2. $H^{1'}$ and $H^{3'}$ are essentially in the plane. Drawings of IV and V are given in Fig. 1a and 1b.

The amount of bending of the H atoms from the plane of the carbon atoms is a function of solvation; it is more pronounced in the unsolvated II than in IV and V because the π-acceptor and σ-donor qualities of Li^+ are stronger than those of

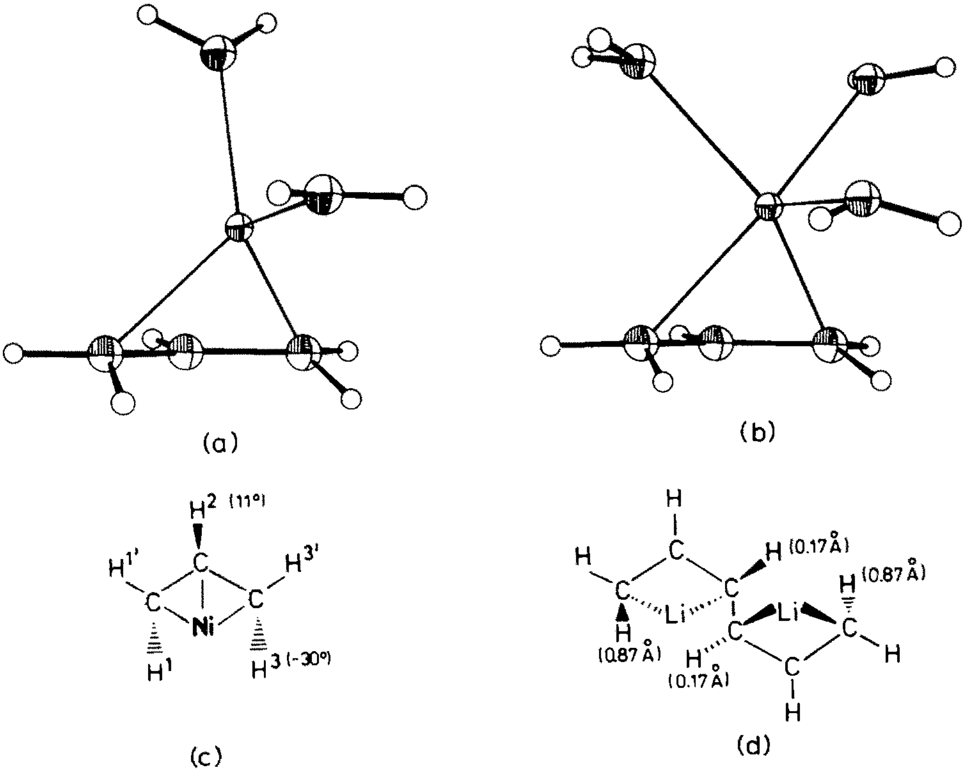


Fig. 1. (a) MNDO geometry optimized structure of IV; (b) MNDO geometry optimized structure of V; (c) one C_3H_5-portion of $(\eta^3\text{-}C_3H_5)_2NiP(CH_3)_3$ [9]; (d) the positions of the H-atoms in $C_6H_8Li_2 \cdot 2TMEDA$ [10] (TMEDA omitted).

$Li^+ \cdot 2(3)H_2O$. Furthermore, stronger solvation leads to higher negative charges in the C_3H_5 component, a widening of the $C^1C^2C^3$angle and a longer distance from the lithium atom to the carbon atoms. Accordingly, without the influence of a counter-ion the planar allyl anion with a rather large $C^1C^2C^3$angle (~ 131°) is formed [3].

Do the results of the MNDO calculations of II–V (and those of the ab initio calculation of II [2] which agree essentially with MNDO) provide a realistic model for the positions of the hydrogens in allyllithium? Until an X-ray structure gives the final answer the structure of IV has to be compared with the structures of other allyl complexes.

In the nickel complex $(\eta^3\text{-}C_3H_5)_2NiP(CH_3)_3$ it is also H^1 and H^3 which are much more bent out of the $C^1C^2C^3$ plane than H^2 [9], s. Fig. 1c; it may be accidental that the out of plane angles of $H^1(H^3)$, H^2 and $H^{1'}$ $(H^{3'})$ agree quite well with those calculated for allyllithium (see **Ia** [2] and II, IV and V in Tab. 2).

Similarly, in the TMEDA complex of the hexatriene dianion $C_6H_8Li_2 \cdot 2TMEDA$, which can be regarded as two allyllithiums attached by a single bond (Fig. 1d), the two inner hydrogens are bent out strongly (0.87 Å) and two outer hydrogens modestly (0.17 Å) of the plane of the carbon atoms; the central hydrogens, corresponding to H^2 in allyllithium, remain in the plane of the carbon atoms [10].

In summary, all the results of the MNDO and ab initio calculations of II–V as well as the X-ray data for related molecules indicate that H^1 and H^3 of allyllithium are much more bent out of the plane of the carbon atoms than H^2. The opposite conclusions drawn from the $^1J(C,H)$ and $^3J(H,H)$ coupling constants of allyllithium in THF would require that the $^1J(C^2H^2)$ coupling constant reflects essentially only the hybridization at this carbon atom. Benn and Rufińska recently pointed out [11], that the small $^1J(C^2H^2)$ coupling constant of allyllithium might be caused by a $C^1C^2C^3$ angle widening, which is supported by all calculations, s. Tab. 2 and ref. 2, 3. That the bond angle $C^1C^2C^3$ does, indeed, strongly influence the $^1J(C^2H^2)$ coupling constant of allyl "anions" will be shown experimentally in a subsequent paper [12].

Acknowledgements

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Note added in proof: After submission of the manuscript we were informed by Prof. Schleyer of a recent publication: "Allyllithium, Allylsodium, and Allylmagnesium Hydride: Geometries and Bonding. A Comparative Ab Initio Study", T. Clark, C. Rohde, and Paul von Ragué Schleyer, Organometallics, in print. The ab initio and the MNDO calculated structures are remarkably similar (s. **Ia** and ref. 2); furthermore, Schleyer et al. reach the same conclusions regarding the out of plane bending of H^2 in allyllithium: the small $^{13}C^2$–H^2 coupling constant must result from the CCC angle widening at C^2 and not from a strong out of plane bending of H^2. We are grateful to Professor Schleyer for sending us the unpublished data.

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